

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-289134

(43)Date of publication of application : 17.10.2000

(51)Int.Cl.

B32B 3/30  
B05D 7/24  
B32B 9/00  
C03C 17/34  
C09D 5/00  
C09D185/00  
C09K 3/18

(21)Application number : 2000-016571

(71)Applicant : NIPPON SHEET GLASS CO LTD

(22)Date of filing : 26.01.2000

(72)Inventor : DOSHITA KAZUHIRO  
INOMATA HIROYUKI  
TSUJINO TOSHIFUMI

(30)Priority

Priority number : 11023573    Priority date : 01.02.1999    Priority country : JP  
11023574    01.02.1999    JP

(54) ARTICLE HAVING HYDROPHILIC SURFACE AND PRODUCTION THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an anti-fog and anti-fouling article excellent in hydrophilicity keeping capacity after the stop of the irradiation with ultraviolet rays and keeping good anti-fog and anti-fouling capacity over a long period of time.

SOLUTION: In an article having a hydrophilic surface having a substrate, the photocatalyst layer applied thereon and the hydrophilic metal oxide layer applied on the photocatalyst layer, the hydrophilic metal oxide layer contains fine particles of hydrophilic metal oxide and a binder of hydrophilic metal oxide and the article has irregularities on its surface.

## \* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

## DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to an article which made hydrophilic nature the base material surface of glass, ceramics, a plastic, or metal, and a manufacturing method for the same.

[0002]

[Description of the Prior Art] In a car and the field of construction, there are mainly strong needs for an antifog antifouling glass plate for many years. Especially in a car, the fog resistance grant to a windowpane from a viewpoint of safe running is becoming an important technical problem.

[0003] Various antifog coating on glass articles from the former has been considered. For example, organicity containing a surface-active agent and/or coating of an inorganic thin film (JP,7-117202,A, method 1), They are coating (JP,1344292,B, method 2) of hydrophilic polymer, coating (JP,6-220428,A, method 3) of the organic inorganic composite membrane containing a hydrophilic organic functional group, etc.

[0004] Although excelled in initial performance, since a surface-active agent is consumed gradually, the described method 1 has the fault that it is short-life. The method 2 is inapplicable to the glass with which the comparatively big mechanical strength of a car, construction, etc. is demanded depending on a use although it is an effective means. The method 3 is devised in order to reconcile antifog performance and a mechanical strength, but all have a limit in respect of performance. When dirt once adheres, the problem of falling remarkably also has antifog performance.

[0005] Then, the antifog antifouling article which covered titanium oxide which is an oxide semiconductor which acts as a photocatalyst to the base material surface was proposed recently (JP,2756474,B, method 4). This uses that the clean surface which has remarkable hydrophilic nature is acquired, as a result of carrying out oxidative degradation of the organic matter which titanium oxide of the surface of glass absorbed ultraviolet radiation, and stuck to the glass surface by the energy efficiently. If all comprise an inorganic substance in material and it excels also in mechanical intensity, and also even ultraviolet radiation hits even if dirt

once adheres, the surface will be defecated again and a hydrophilic surface will revive. If the surface maintains hydrophilic nature, the oleophilic black dirt which is city type dirt is not attached easily, moreover -- the attached dirt is removed by the rainfall -- easy (for example, smallness Toshiki Matsuzawa.) Nakaya Toshikazu, a "new preventable contamination type paint", paint art, the January, 1995 item, 94-99 (1995); Tanaka Shoichi, "contamination degradation and contamination-resistant paint art (industrial use paint)", paint art, the October, 1996 special number item, 95-102 (1995). It has what is called self-cleaning nature, and can be used as an antifouling material.

[0006]As an example of the article which has a hydrophilic surface using photocatalysts, such as this titanium oxide, What mixed silica etc. with the photocatalyst (for example, JP,2756474,B), the thing (for example, JP,2865065,B, JP,10-57817,A) in which metallic compound layers, such as silica, were formed on the photocatalyst layer, etc. are proposed.

[0007]Metallic oxides (for example, molybdenum, the oxide of tungsten) other than silica, The thing which the photocatalyst layer was made to contain, or the thing (JP,10-147770,A, JP,10-152346,A) made to form as a surface layer on a photocatalyst layer is also proposed as a member which can maintain fog resistance over a long period of time (method 5).

[0008]To JP,10-36144,A, the antifog element forms the film of a hydrophilic metallic oxide like silica to porous state, and the porous opening was made to reach on the photocatalyst membrane of the surface of a transparent substrate member at a photocatalyst layer is indicated (method 6). Thus, the organic matter etc. which entered into the porous opening when it was made to reach a photocatalyst layer carry out direct contact of the porous opening to photocatalyst membrane, and a photocatalysis decomposes, it is removed, and fog resistance is maintained over a long period of time.

[0009]

[Problem(s) to be Solved by the Invention]However, these articles based on the method 4 and the method 6 were not enough as the hydrophilic maintenance performance (maintenance performance of the hydrophilic nature after stopping UV irradiation) of the surface hydrophilic-nature-ized by UV irradiation, and there was a problem which maintenance of performance said was not so good especially about fog resistance. It originated in this and there were antifouling property, self-cleaning nature, and a problem said that it is not enough and the antifouling performance of a part in which light seldom hits is not enough.

[0010]Although the method 5 is combining a photocatalyst, metal, or its oxide and it aims at raising photocatalyst activity and maintaining fog resistance over a long period of time, if various metallic compounds are added to a photocatalyst layer, problems, such as membranous transparency and a fall of a mechanical strength, will arise.

[0011]This invention is excellent in the maintenance performance of the hydrophilic nature after stopping UV irradiation in view of the above-mentioned conventional technology, It aims at providing the antifog antifouling article which has the outstanding antifog antifouling performance which can maintain for example, use the good antifog antifouling performance over a long period of time for a car and the windowpane of a building, a mirror, an optic, glasses, etc.

[0012]

[Means for Solving the Problem]As a result of inquiring wholeheartedly that this invention persons should attain the above-mentioned purpose, particles of hydrophilic metallic oxides, such as oxidized silicon, are adhered with a binder of a hydrophilic metallic oxide on photocatalyst layers, such as titanium oxide, When it found out that hydrophilic nature produced by UV irradiation would be maintained over a long period of time even in a dark place if an uneven layer is formed and said uneven layer was formed in island shape, the shape of a film in which a hole opened, and mesh shape, further, it found out that hydrophilic nature was recovered also by weak ultraviolet rays, and this invention was completed.

Membranous transparency and a mechanical strength also have the feature in a place secured simultaneously by not adding particles of a hydrophilic metallic oxide directly to a photocatalyst layer, but making it fix via a binder of a hydrophilic metallic oxide on a photocatalyst layer.

[0013]Namely, in an article which has a layer of a hydrophilic metallic oxide with which this invention was covered on a substrate, a photocatalyst layer with which it was covered on it, and said photocatalyst layer and which has a hydrophilic surface, It is an article which has a hydrophilic surface, wherein said article has unevenness on the surface, including a binder of a hydrophilic metallic oxide for a layer of said hydrophilic metallic oxide to adhere particles and particles of a hydrophilic metallic oxide to said photocatalyst layer.

[0014]As a photocatalyst layer in this invention, a layer of metal oxide semiconductors, such as  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{SnO}_2$ ,  $\text{SrTiO}_3$ ,  $\text{WO}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ , and  $\text{MoO}_2$ , can be mentioned. In these, catalytic activity is high and titanium oxide ( $\text{TiO}_2$ ) which has the outstanding physicochemical stability is used preferably.

[0015]Formation of a photocatalyst layer is performed using a usual thin-film-fabrication method, and it is not limited in particular. However, even if it coats a glass substrate surface with photocatalyst membrane like titanium oxide membrane directly, high photocatalyst activity may not be acquired. This is because alkali metal ion, such as Na ion which were spread and came out out of a glass base material containing an alkaline metal on the occasion of heat treatment, combines with titanium oxide and the crystallinity of titanium oxide in a film is reduced. When a glass material which contains an alkaline metal as a substrate is used, in order to prevent a fall of the crystallinity of this titanium oxide membrane, another oxidized silicon film and alkali interception film is provided in a glass base material, and photocatalyst membrane containing titanium oxide is coated on it.

[0016][Alkali interception film] What consists of a single ingredient or a multicomponent presentation chosen from oxidized silicon, an aluminum oxide, titanium oxide, zirconium oxide, and a group that consists of cerium oxide as the above-mentioned alkali interception film is used suitably. In these, a multicomponent thing an oxidized silicon (silica) single ingredient or whose main ingredients are oxidized silicon is preferred, and it is still more preferred that they are oxidized silicon and a two-component system metallic oxide of zirconium oxide. A metallic oxide whose main ingredients are oxidized silicon can be formed without a refractive index spoiling the optical characteristic of a glass plate greatly low, and is preferred, In oxidized

silicon and a two-component system metallic oxide of zirconium oxide, since alkali cutoff performance is dramatically high, it is still more desirable, and especially content of zirconium oxide has preferred 1-% of the weight or more 30 or less % of the weight of thing. When content is lower than 1 % of the weight, an alkali cutoff performance improved effect does not not much have a difference with an oxidized silicon simple substance, Since a tendency for improvement in reflectance not only by an alkali cutoff performance improved effect not improving any longer but refractive-index increase to take place will become strong and will become difficult to control the optical characteristic of a glass plate if higher than 30 % of the weight, it is not desirable.

[0017]As for thickness of the above-mentioned alkali interception film, it is preferred that it is [ not less than 5 nm ] 300 nm or less. If thickness is thinner than 5 nm, an alkali screening effect is not enough, and since an interference color by a film will come to be accepted notably and will become difficult to control the optical property of a glass plate if thicker than 300 nm, it is not desirable.

[0018]The above-mentioned alkali interception film can be formed by a publicly known method. for example, a sol gel process (for example, Yuji Yamamoto, Kan-ichi Kamiya, Sumio Sakuhana, and a ceramic industry association magazine.) 90, 328-333 (1982), liquid phase deposition (for example, JP,1-59210,B, JP,4-13301,B), Vacuum film formation method (vacuum deposition, weld slag), a burning method and the spray coat (for example, JP,53-124523,A, JP,56-96749,A), a CVD method (for example, JP,55-90441,A, JP,1-201046,A, JP,5-208849,A), etc. can be illustrated.

[0019][Photocatalyst layer] A photocatalyst layer in this invention is produced using a usual thin-film-fabrication method, for example, can illustrate a sol gel process, liquid phase deposition (for example, JP,2716244,B), vacuum film formation method (vacuum deposition, weld slag), a burning method and the spray coat, a CVD method, etc.

[0020]Catalytic activity of a photocatalyst layer is high, and as for a photocatalyst layer in this invention, although titanium oxide which has the outstanding physicochemical stability is used preferably, it is preferred to contain a titanium oxide crystal 30 to 100%. Since photocatalyst activity is not enough if there is less titanium oxide than 30%, hydrophilic nature-ized speed by optical exposure becomes small, and as a result, maintenance performance of hydrophilic nature becomes less good, and is not preferred. As an example of a substance which can be made to contain besides the above-mentioned titanium oxide crystal in a photocatalyst layer, Oxidized silicon, an aluminum oxide, an alkaline metal, zirconia, antimony oxide, Amorphous titanium oxide and hydrous titanium oxide, aluminum, manganese,  $\text{GeO}_2$ ,  $\text{ThO}_2$ ,  $\text{ZnO}$ ,  $\text{SnO}_2$ ,  $\text{SrTiO}_3$ ,  $\text{WO}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{MoO}_2$ ; Magnesium (Mg), A compound of scandium (Sc) and vanadium (V), chromium (Cr), manganese (Mn), yttrium (Y), niobium (Nb), molybdenum (Mo), a ruthenium (Ru), tungsten (W), and a rhenium (Re) can be mentioned. As for these additive content, 1 to 70 % of the weight is preferred.

[0021]As for thickness of this photocatalyst membrane, it is preferred that it is 2-500 nm. Since light cannot fully be absorbed but antifog antifouling performance will become low if thickness

is thinner than 2 nm, it is not desirable. An interference color is accepted notably and is not preferred except that photocatalyst activity will fall and antifog antifouling performance will fall as a result, since an optical carrier produced in a film cannot be spread to a membranous outer surface if thickness is thicker than 500 nm. Antifog antifouling durability in case light does not hit that thickness is not less than 20 nm becomes still higher, and abrasion resistance becomes it still higher that thickness is 200 nm or less. Therefore, thickness of more desirable photocatalyst membrane is 20-200 nm.

[0022][Overcoat layer] in this invention, a layer (it is henceforth called an overcoat layer) of a hydrophilic metallic oxide covered on a photocatalyst layer, With a binder of a hydrophilic metallic oxide for adhering to said photocatalyst layer, particles and particles of a hydrophilic metallic oxide are formed in a form of a concavo-convex film on said photocatalyst layer.

[0023]Although this overcoat layer may be formed in a form of an uneven layer which covered said photocatalyst layer thoroughly, it is preferred to have an opening which is formed on said photocatalyst layer in a form of an uneven layer of island shape, the shape of a film in which a hole opened, or mesh shape, and reaches a photocatalyst layer.

[0024]As particles of the above-mentioned hydrophilic metallic oxide which constitutes an overcoat layer, A metal oxide particle of a single ingredient chosen from a group which consists of oxidized silicon, an aluminum oxide, titanium oxide, zirconium oxide, molybdenum oxide, vanadium oxide, and cerium oxide, and composite metal oxide particles which consist of these mixtures and two or more sorts of these ingredients are used. As for particle diameter of a hydrophilic metal oxide particle, not less than 4 nm 300 nm or less is preferred. By using particles of particle diameter of this range, surface unevenness after overcoat layer formation becomes a suitable value, and maintenance performance of hydrophilic nature improves more. In use of particles smaller than 4 nm, it can be hard to form required unevenness on the surface of an overcoat layer, Since arithmetic mean roughness (Ra) of surface unevenness is set to less than 0.5 nm, a tendency for transparency to be undesirably spoiled by overcoat layer formation by use of larger particles than 300 nm is not strongly preferred.

[0025]As the above-mentioned hydrophilic metal oxide particle, chain particles are preferred. Since an overcoat layer becomes the surface of uneven shape complicated on a three-dimensional solid target by using chain-shaped particles, Since it becomes easy to form an opening which can form antifog performance and high surface unevenness shape of antifog durability, and reaches an overcoat layer at a photocatalyst layer, the shape of surface type whose antifog performance and antifog durability are still higher can be formed. as the example of chain colloid -- silica by Nissan Chemical Industries, Ltd. -- "SNOWTEX OUP" and "SNOWTEX UP" which are sol are mentioned, and these have a diameter of 10-20 nm, and a length of 40-300 nm.

[0026]As a binder of a hydrophilic metallic oxide which constitutes an overcoat layer, It is preferred that they are at least one sort of metallic oxides chosen from oxidized silicon, an aluminum oxide, cerium oxide, zirconium oxide, molybdenum oxide, vanadium oxide, and amorphous titanium oxide, and it contains oxidized silicon 50% of the weight or more more preferably. If oxidized silicon is included 50% of the weight or more, an improved effect of

hydrophilic nature is remarkable.

[0027]To an overcoat layer, aluminum (aluminum), magnesium (Mg), Iron (Fe), scandium (Sc), and vanadium (V), chromium (Cr), Manganese (Mn), yttrium (Y), niobium (Nb), molybdenum (Mo), By adding a ruthenium (Ru), tungsten (W), and a compound of a rhenium (Re), for example, oxide particles of these metal, (however, a different substance from said hydrophilic metal oxide particle used), Condensation of a hydrophilic metallic oxide can be promoted, and uneven shape good as a result can be formed, and an overcoat layer of island shape, the shape of a film in which a hole opened, or mesh shape can be formed easily. Although an addition in particular of these compounds is not limited, 0.01 to 50 % of the weight is preferred. if less than 0.01 % of the weight, an effect of addition is not enough, and if more than 50 % of the weight, since a mechanical strength of an overcoat layer will fall, it is not desirable. Among the above and an additive, since aluminum (aluminum), magnesium (Mg), iron (Fe), and vanadium (V), niobium (Nb), and molybdenum (Mo) make high especially hydrophilic nature of the overcoat layer itself other than an effect of the above-mentioned addition, they are used especially preferably.

[0028]As for thickness of this overcoat layer, it is preferred that it is 0.01-50 nm in average thickness. Since an effect of overcoat will be low, namely, hydrophilic performance will not improve if average thickness is thinner than 0.01 nm, it is not desirable. Since hydrophilic nature or fog resistance recovery performance by optical exposure falls, and membranous intensity will fall even if it is hard to become island shape, the shape of a film in which a hole opened, or mesh shape and can give such a gestalt if average thickness is thicker than 50 nm, it is not desirable. Since abrasion resistance will become still higher if antifog durability will improve further if average thickness shall be 0.1 nm or more, and it is made 20 nm or less, average thickness of 0.1-20 nm is more preferred.

[0029>About content of a hydrophilic metal oxide particle which constitutes an overcoat layer, and a hydrophilic metallic-oxide binder. When there is not much too little content of a hydrophilic metallic-oxide binder, it becomes insufficient pasting up of a hydrophilic metal oxide particle, an overcoat layer becomes weak (when there is too much hydrophilic metal oxide particle content), and a mechanical strength, especially abrasion resistance fall. When there is not much too much quantity of a binder of a hydrophilic metallic oxide conversely (when there is too little hydrophilic metal oxide particle content), When you are going to make it form an overcoat layer of the shape of a film in which formation of a rugged form overcoat gestalt was not enough for, and a hole opened, or mesh shape, Since a binder fills a gap between hydrophilic metal oxide particles and an opening does not remain, it becomes difficult to form an opening into an overcoat layer. Therefore, it is preferred that a hydrophilic metal oxide particle contains 95 or less % of the weight 5% of the weight or more in said overcoat layer. As for content of a binder of a hydrophilic metallic oxide, in other words, it is preferred that it is 5 to 1900 % of the weight to weight of a hydrophilic metal oxide particle. It is 5 to 400 % of the weight more preferably, and is 50 to 200 % of the weight still more preferably.

[0030]As for surface unevenness of an overcoat layer, it is preferred that arithmetic mean roughness (Ra) is 0.5-100 nm, and a concavo-convex average interval (Sm) is 4-300 nm. Even

if a Ra value is smaller than 0.5 nm and it is larger than 100 nm, neither antifog performance nor antifog durability is low preferred. Even if Sm value is smaller than 4 nm and it is larger than 300 nm, too, antifog performance and antifog durability are low and are not preferred. If especially Sm value is larger than 300 nm, since transparency will be spoiled, it is not desirable. Surface unevenness of an overcoat layer of this invention is still more preferred, arithmetic mean roughness (Ra) is 5-30 nm, and a concavo-convex average interval (Sm) is 5-150 nm. Antifog performance, especially antifog durability are still better in this range.

[0031]A Ra value and Sm value are defined by a method of JIS B 0601 (1994) statement here, An atomic force microscope (for example, SPI3700 by SEIKO electronic incorporated company) and an electron microscope (for example, Hitachi Make H-600) are calculable from a profile curve used and measured [ observed and ].

[0032]In a form of an island, in an overcoat layer of island shape, a particle of a hydrophilic metallic oxide or its floc separated an interval mutually, has adhered on the surface of a photocatalyst layer, and a binder of a hydrophilic metallic oxide, A particle of a hydrophilic metallic oxide or its floc is pasted up on a photocatalyst layer, or the particles of a hydrophilic metallic oxide are pasted up. It exposes and surface portions other than a portion to which a particle of a hydrophilic metallic oxide or its floc has adhered among the surfaces of a photocatalyst layer are well-informed about the open air through an opening of an overcoat layer. As for an average diameter of an island, it is preferred that it is 5-500 nm.

[0033]In an overcoat layer of the shape of a film in which a hole opened, or mesh shape. A particle of a hydrophilic metallic oxide or its floc has adhered on the surface of a photocatalyst layer, being connected mutually, and a binder of a hydrophilic metallic oxide, A particle of a hydrophilic metallic oxide or its floc is pasted up on a photocatalyst layer, or the particles or the flocs of those of a hydrophilic metallic oxide is pasted up. It exposes and surface portions other than a portion to which a particle of a hydrophilic metallic oxide or its floc has adhered among the surfaces of a photocatalyst layer are well-informed about the open air through a hole or a meshes-of-a-net opening (breakthrough) of an overcoat layer. As for an average diameter of a hole or a meshes-of-a-net opening, it is preferred that it is 5-500 nm.

[0034]Thus, in having an opening which an overcoat layer is formed on a photocatalyst layer in a form of an uneven layer of island shape, the shape of a film in which a hole opened, or mesh shape, and reaches a photocatalyst layer. Since the surface of a photocatalyst layer is covered with a hydrophilic metallic oxide by the part and other portions are not covered with a hydrophilic metallic oxide, the photocatalyst activity of a photocatalyst layer does not fall greatly. Therefore, decomposition performance, and hydrophilic nature and fog resistance recovery performance by optical exposure of surface dirt by optical exposure are maintained with improvement in hydrophilic nature by overcoat formation, without being spoiled greatly.

[0035]Hydrophilic nature and fog resistance recovery performance by optical exposure may improve rather than overcoat formation before by formation of an overcoat layer which has an opening which reaches a photocatalyst layer. Although this cause is unknown, silica is contained in an overcoat layer, and when titanium oxide is contained in a photocatalyst layer, it accepts in many cases.



[0036]And it is preferred for 10 to 90% of surface portion of surface area of said photocatalyst layer to be exposed, and to face an opening of a layer of said hydrophilic metallic oxide. With exposed surface area being not less than 10%, a photocatalyst activity fall is small and decomposition performance, and hydrophilic nature and fog resistance recovery performance by optical exposure of surface dirt by optical exposure improve. Conversely, an improved effect of hydrophilic nature according that exposed surface area is 90% or less to overcoat layer formation is remarkable. The more desirable exposed surface area percentage is 30 to 70%. In this range, hydrophilic improvement by overcoat layer formation and hydrophilic recovery performance by photocatalyst layer exposure can be balanced, and it is the most desirable.

[0037]It consists of particles of a hydrophilic metallic oxide, and a binder of a hydrophilic metallic oxide, a crevice (space) arises between an adjacent particle and its floc, and an overcoat layer which has an opening which reaches a photocatalyst layer forms an opening. In order for the photocatalyst activity of a photocatalyst layer to act effectively and to result in improvement in decomposition performance of surface dirt, Not only an exposed surface area rate of the above-mentioned photocatalyst layer but an opening or an opening in an inside of an overcoat layer is important, Volume of an overcoat layer. (The maximum heights of the surface of a photocatalyst layer, and an overcoat layer.) it measures in space between fields to connect -- it being preferred that it is 10 to 90%, and for the same reason as an exposed surface area rate of the comparatively (W/V) above-mentioned photocatalyst layer of the opening W in V (value which lengthened the volume X of particles of a hydrophilic metallic oxide, and a binder of a hydrophilic metallic oxide from V), It is still more preferred that it is 30 to 70%.

[0038]Although it is produced using a publicly known thin-film-fabrication method, for example, a sol gel process, liquid phase deposition, a burning method and the spray coat, a CVD method, etc. can be illustrated, since a sol gel process tends to adjust a surface shape of an overcoat layer, covering of said overcoat layer is used preferably.

[0039]. As a method of forming said overcoat layer, a hydrophilic metallic oxide can be formed, respectively. In liquid containing at least one sort chosen from a group which consists of an organic metallic compound in which hydrolyzed condensation polymerization is possible, chlorosilyl group content compounds, and those hydrolyzates. A method (henceforth a method (A)) of forming by applying liquid which may have a hydrophilic metal oxide particle added on a substrate in which said photocatalyst layer was formed can be illustrated.

[0040]As an organic metallic compound which can form a hydrophilic metallic oxide in the above-mentioned formation method and in which hydrolyzed condensation polymerization is possible, an organic metallic compound of silicon, aluminum, titanium, a zirconium, molybdenum, vanadium, or cerium is used. As the above-mentioned hydrophilic oxide particles, oxidized silicon, an aluminum oxide, A metal oxide particle of a single ingredient chosen from a group which consists of titanium oxide, zirconium oxide, molybdenum oxide, vanadium oxide, and cerium oxide, and composite metal oxide particles which consist of these mixtures and two or more sorts of these ingredients are used. These are preferably used in a

form of solvent distribution sol (colloidal solution). However, since a metallic oxide obtained does not show hydrophilic nature, an organic metallic compound of titanium and combination of titanium oxide particles are unsuitable.

[0041]as the solvent distribution sol of the above-mentioned metallic oxide -- for example, silica by Nissan Chemical Industries, Ltd. -- "SNOWTEX OL" who is sol. "SNOWTEX O", "SNOWTEX OUP", and "SNOWTEX UP", the company's alumina sol "alumina sol 520" and the company's zirconia -- sol "NZS-30A". a titania by Ishihara Sangyo Kaisha, Ltd. -- sol "CS-N" and "STS-01". ceria by "STS-02" Taki Chemical Co., Ltd. -- sol "Knee Doral U-15". a titania -- "IPA-ST" by Nissan Chemical Industries, Ltd. besides commercial water dispersed sols, such as sol "M-6",. commercial organic solvent distribution silica like "XBA-ST" -- a commercial water alcoholic partially aromatic solvent distribution titania having contained a binder as shown in sol, "ST-K01" by Ishihara Sangyo Kaisha, Ltd., and "ST-K03" -- sol etc. are mentioned.

[0042]A dispersing solvent of the above-mentioned metal oxide particle will not be limited in particular, if a metal oxide particle is distributing stably substantially, but its simple substance or mixtures, such as water, methanol, ethanol, and propanol, are preferred, and its water is still more preferred. Since these water and lower alcohol are simply mixed with a solution containing the above-mentioned organic metallic compound and heat treatment after desiccation and membrane formation at the time of membrane formation can remove them easily, they are good. Among these, water is the most preferred on manufacturing environment.

[0043]When adding the above-mentioned metal oxide particle in a solution containing the above-mentioned organic metallic compound and a chlorosilyl group content compound, a distributed auxiliary agent may be added. . A distributed auxiliary agent in particular is not limited, but, generally are used as a distributed auxiliary agent. For example, electrolytes, such as sodium phosphate, hexametaphosphoric acid sodium, potassium pyrophosphate, an aluminium chloride, and ferric chloride, various surface-active agents, various organic high polymers, a silane coupling agent, a titanium coupling agent, etc. are used. The addition is usually 0.01 to 5 % of the weight to the above-mentioned metal oxide particle.

[0044]As an organic metallic compound which can form a hydrophilic metallic oxide included in coating liquid for overcoat layer formation with the above-mentioned metal oxide particle and in which hydrolyzed condensation polymerization is possible, As long as it performs hydrolysis and dehydration condensation, what kind of compound may be fundamentally sufficient, but a metal alkoxide and a metal chelate are preferred.

[0045]Specifically, methoxides, such as silicon, aluminum, a zirconium, and titanium, ethoxide, propoxide, butoxide, etc. are preferably used as a simple substance or a mixture as a metal alkoxide. As a metal chelate, acetylacetonate complexes, such as silicon, aluminum, a zirconium, and titanium, are used preferably.

[0046]As an alkoxide of silicon, the alkyl silicate 40, for example, "ethyl silicate" by col coat incorporated company, and "MS56" by Mitsubishi Chemical, Inc. etc. can be used. [ amount of polymers type ] As hydrolyzate of an alkoxide of silicon, commercial alkoxysilane hydrolyzing

liquid, For example, made in a "HAS-10", Inc. by col coat incorporated company date-plate research institute "Serra Mika G-91", "Serra Mika G-92-6", and "ATORON NSI-500" by Nippon Soda Co., Ltd. etc. can be used.

[0047]With a chlorosilyl group content compound which is included in coating liquid for overcoat layer formation with the above-mentioned hydrophilic metal oxide particle and which can form a hydrophilic metallic oxide. it is a compound which has at least one chlorosilyl group ( $n$  is 1, 2, or 3 in  $-\text{SiCl}_n\text{X}_{3-n}$  and here --  $\text{X}$  -- hydrogen -- or a carbon number is an alkyl group, an alkoxy group, or an acyloxy group of 1-10, respectively) in intramolecular. Also in it, a compound which has at least two chlorine is preferred, and chlorine replaces at least two hydrogen in Silang  $\text{Si}_n\text{H}_{2n+2}$  ( $n$  is an integer of 1-5 here), Chlorosilane which replaced other hydrogen with the above-mentioned alkyl group, an alkoxy group, or an acyloxy group if needed, and its condensation polymer are preferred.

[0048]For example, tetrachlorosilane (a silicon tetrachloride,  $\text{SiCl}_4$ ), trichlorosilane ( $\text{SiHCl}_3$ ), Trichloro monomethyl silane ( $\text{SiCH}_3\text{Cl}_3$ ), dichlorosilane ( $\text{SiH}_2\text{Cl}_2$ ), and  $\text{Cl}-(\text{SiCl}_2\text{O})_n-\text{SiCl}_3$  ( $n$  is an integer of 1-10) etc. can be mentioned. Hydrolyzate of the above-mentioned chlorosilyl group content compound can also be used, and out of these, it is independent or can be used combining plurality. The most desirable chlorosilyl group content compound is tetrachlorosilane. Since reactivity is dramatically high, the chlorosilyl group can form a precise tunic by carrying out self-condensation or a base material surface, and a condensation reaction.

[0049]A solvent of a solution containing the above-mentioned organic metallic compound, chlorosilyl group content compounds, or those hydrolyzates is [ anything ] fundamentally good if the above-mentioned organic metallic compound, chlorosilyl group content compounds, or those hydrolyzates are dissolved substantially. Alcohols, such as methanol, ethanol, propanol, and butanol, can be the most preferred, and the sum total of the above-mentioned organic metallic compound, chlorosilyl group content compounds, and those hydrolyzates can be made to specifically contain by 1 to 30% of the weight of concentration.

[0050]Water is required for hydrolysis of the above-mentioned organic metallic compound. Although acid and neutral any may be sufficient as this, in order to promote hydrolysis, water which is chloride, nitric acid, sulfuric acid, acetic acid, citrate, sulfonic acid, etc. which have a catalysis, and was made into acidity is used preferably.

[0051]As for an addition of water required for hydrolysis of the above-mentioned organic metallic compound, 0.1-100 are good to an organic metallic compound at a mole ratio. If there are few water additions at a mole ratio than 0.1, promotion of hydrolysis of an organic metallic compound is not enough, and if more than 100 at a mole ratio, it becomes the tendency for the stability of liquid to fall and is not desirable.

[0052]Although an addition in particular of acid is not limited, 0.001-20 are good to an organic metallic compound at a mole ratio. If there is less addition acidity at a mole ratio than 0.001, promotion of hydrolysis of an organic metallic compound is not enough, and it is not desirable, and if more than 20 at a mole ratio, the acidity of liquid becomes strong too much and is not

preferred on handling. From a viewpoint of only hydrolysis, a maximum of addition acidity is 2 in a mole ratio to an organic metallic compound. Even if acidity increases more, a grade of advance of hydrolysis seldom changes. However, a film to which membranous intensity increases remarkably and desiccation at low temperature (room temperature -250 \*\*) can also be equal to practical use enough by many acid addition from this may be obtained.

[0053] Acid is [ 0.0001-2.0mol/L, and moisture of concentration of a metallic oxide in which a desirable presentation of coating fluid in which increase of such film strength is accepted is converted from an organic metallic compound or its hydrolyzate ] 0.001 to 20 % of the weight 0.00001 to 0.6% of the weight.

[0054] A desirable presentation of coating fluid in a case of making a layer of a hydrophilic metallic oxide cover with the state of having an opening which reaches a photocatalyst layer, Acid is [ 0.0001-1.0mol/L, and moisture of concentration of a metallic oxide converted from an organic metallic compound or its hydrolyzate ] 0.001 to 10 % of the weight 0.00001 to 0.3% of the weight. And a desirable presentation of coating fluid in a case of making a layer of a hydrophilic metallic oxide which does not have an opening which reaches a photocatalyst layer cover, Acid is [ 0.1-2.0mol/L, and moisture of concentration of a metallic oxide converted from an organic metallic compound or its hydrolyzate ] 0.01 to 20 % of the weight 0.01 to 0.6% of the weight.

[0055] Acid used at this time has nitric acid or preferred chloride, and it is preferred to use acid which has concentration of 0.3 time or more of a moisture content. That is, when using acid of a form of solution, it is preferred that it is high-concentration acid which has not less than 23.1% of concentration. If an ethanol solution contains 0.5% of the weight of moisture when using acid in a form of an ethanol solution, that whose concentration of acid in an ethanol solution is 0.15 % of the weight or more is preferred.

[0056] To use the above-mentioned chlorosilyl group content compound, neither water nor acid necessarily needs to be added. Even if it adds neither water nor acid at all additionally, hydrolysis advances with moisture contained in a solvent, moisture in atmosphere, etc. Chloride separates in liquid with this hydrolysis, and hydrolysis advances further. However, even if it adds water and acid additionally, it does not interfere at all.

[0057] The above-mentioned organic metallic compound, chlorosilyl group content compounds, or those hydrolyzates can be mixed with the above-mentioned metal oxide particle with a solvent, water, an acid catalyst, and a distributed auxiliary agent can be added if needed, and coating fluid for forming an overcoat layer on a substrate can be prepared. At this time, an organic metallic compound and a chlorosilyl group content compound may be used independently, or it may mix, and they may be used, or whichever may be sufficient as them. A desirable raw material compounding ratio of this coating fluid is as in the next table 1. As for the amount of solvents in front, when making a layer of a hydrophilic metallic oxide which does not have an opening which reaches a photocatalyst layer cover, it is preferred that it is 500 to 3000 weight section.

[0058]

[Table 1]

----- An organic metallic compound or chlorosilyl group content compound Or those hydrolyzate 100 weight sections of the Ten to metal oxide particle 200 weight section Zero to water 150 weight section Zero to acid catalyst 35 weight section 0.001 to distributed auxiliary agent 10 weight section 500 to solvent 300000 weight section. -----

-----[0059]The above-mentioned organic metallic compound or a chlorosilyl group content compound is melted in a solvent, a catalyst and water are added, and it hydrolyzes for two days from for 5 minutes at a predetermined temperature during the boiling point of 10 \*\* and a solution. Add a distributed auxiliary agent there a metal oxide particle and if needed, it is made to react for two days from for 5 minutes at a predetermined temperature during the boiling point of 10 more \*\* and a solution if needed, and coating fluid for overcoat layer formation is obtained.

[0060]When using a chlorosilyl group content compound, it is not necessary to add a catalyst and water specially. A metal oxide particle may be added before the above-mentioned hydrolysis process. In order to skip the hydrolysis process of an organic metallic compound, the organic metallic compound hydrolyzate solution of the above-mentioned marketing may be used. The obtained coating fluid may be diluted with a suitable solvent according to a coating method after that.

[0061]On the photocatalyst layer which consists of titanium oxide etc., it can apply and dry, the above-mentioned coating fluid for overcoat layer formation can be heat-treated if needed, and the layer of the hydrophilic metallic oxide thoroughly covered or covered with the state of having an opening which reaches on a photocatalyst layer at a photocatalyst layer can be formed.

[0062]Although publicly known art should just be used for the method of the above-mentioned spreading and it is not limited in particular, Various print processes, such as methods, such as a method of using devices, such as a spin coater, a roll coater, a spray coater, and a curtain coating machine, the immersion Czocharski method (the dip-coating method), a flow-coating method (the flow coating method), screen-stencil, gravure printing, curved surface printing, are used.

[0063]As for the substrate after spreading, it is preferred to heat-treat from 5 seconds at the temperature between 150 \*\* and substrate heat-resistant temperature after [ from for 1 minute ] 2-hour desiccation for 5 hours if needed with the temperature between 150 \*\* from a room temperature.

[0064]Substrate heat-resistant temperature is a maximum temperature which can hold the characteristic of a parenchyma top substrate, and if it is a glass base material, for example softening temperature, devitrification temperature (usually 600-700 \*\*), etc. are plastics base materials, a glass transition point, crystallization temperature, a decomposition point, etc. will be mentioned, for example.

[0065]By the above-mentioned desiccation or heat treatment, the uneven layer of island shape, the shape of a film in which the hole opened, or mesh shape, or the overcoat layer of uneven shape covered thoroughly can be formed in the photocatalyst layer surface. This overcoat layer consists of a matrix (or binder) of a hydrophilic metal oxide particle and a

hydrophilic metallic oxide (it originates in an organic metallic compound or a chlorosilyl group content compound). The film gestalt presented the rugged form in which the metallic-oxide matrix gathered focusing on the metal oxide particle, and in the uneven layer of the shape of a film in which island shape or a hole opened, or mesh shape, the photocatalyst layer was not covered thoroughly but is exposed in part.

[0066] Thus, the wettability of the article in which the metallic-oxide overcoat layer was formed on the photocatalyst layer surface to water is improving, and the angle of contact of waterdrop has the antifog performance small. Also with some surface dirt, an angle of contact does not go up easily, but it has antifog durability.

[0067] The above the liquid produced by adding a hydrophilic metal oxide particle in the liquid containing the organic metallic compound etc. which can form a hydrophilic metallic oxide, and in which hydrolyzed condensation polymerization is possible mainly as a method of forming said overcoat layer, Although how to form by applying on the substrate in which said photocatalyst layer was formed was indicated, the layer of a rugged form hydrophilic nature metallic oxide can be formed by the two following methods (B) and (C) besides it.

[0068] (B) The organic metallic compound which can form a hydrophilic metallic oxide, respectively and in which hydrolyzed condensation polymerization is possible, How to form by applying the liquid produced by adding an organic polymer compound in the liquid containing at least one sort chosen from the group which consists of chlorosilyl group content compounds and those hydrolyzates on the substrate in which said photocatalyst layer was formed, and carrying out decomposition removal of the organic polymer compound by heat treatment.

(C) The organic metallic compound which can form a hydrophilic metallic oxide, respectively and in which hydrolyzed condensation polymerization is possible, How to form by applying the liquid produced by adding organic polymer particles in the liquid containing at least one sort chosen from the group which consists of chlorosilyl group content compounds and those hydrolyzates on the substrate in which said photocatalyst layer was formed, and carrying out decomposition removal of the organic polymer particles by heat treatment.

[0069] A described method (B) is explained. The metallic-oxide overcoat layer in a method (B) is the same as the method (A) of using the liquid which added the above-mentioned hydrophilic metal oxide particle except the metal oxide particle not being added.

[0070] Although the metal oxide particle is not included, fundamentally in the same coating fluid for overcoat formation as a method (A), At least one sort of organic polymer compounds chosen from the group which consists of a polyethylene glycol, a polypropylene glycol, and polyvinyl alcohol are added, By applying and drying on said substrate formed [ photocatalyst layer ], heating the liquid produced by making dissolve these at further 350-650 °C for for 5 minutes to 2 hours, and disassembling the added organic polymer compound, The uneven layer of island shape, the shape of a film in which the hole opened, or mesh shape, or the overcoat layer of uneven shape covered thoroughly is obtained.

[0071] Said organic polymer compound is added 300 or less % of the weight 30% of the weight or more to the oxide conversion total solids in said coating fluid for overcoat formation. If there are few additions than 30 % of the weight, it is not enough, and concavo-convex

morphogenesis cannot contribute to improvement in hydrophilic nature and also antifog antifouling performance, and is not preferred. If there are more additions than 300 % of the weight, in order to produce the overcoat in which a membranous mechanical strength falls and film formation efficiency is bad and is preferred, it is not desirable too for the reasons of an organic high polymer becoming so much required, and cost starting too much.

[0072]As explained also by said method (A), by adding a lot of acid also by a method (B) in the liquid containing an organic metallic compound, the intensity of the film after membrane formation increases remarkably, and the film to which desiccation at low temperature (room temperature -250 \*\*) is also equal to practical use enough may be obtained.

[0073]The desirable presentation (however, since organic polymer compound content is ending with description, it is removed) of the coating fluid in which increase of such film strength is accepted, Acid is [ 0.0001-2.0mol/L, and the moisture of the concentration of the metallic oxide converted from an organic metallic compound or its hydrolyzate ] 0.001 to 20 % of the weight 0.00001 to 0.6% of the weight.

[0074]The desirable presentation in the case of making the layer of a hydrophilic metallic oxide cover with the state of having an opening which reaches a photocatalyst layer, The concentration of the metallic oxide converted from an organic metallic compound or its hydrolyzate, 0.00001 to 0.3% of the weight, acid is 0.001 to 10 % of the weight, and 0.0001-1.0mol/L, and moisture a still more desirable presentation, Acid is [ 0.01-0.3mol/L, and the moisture of the concentration of the metallic oxide converted from an organic metallic compound or its hydrolyzate ] 0.001 to 3 % of the weight 0.001 to 0.1% of the weight. And acid is [ 0.1-2.0mol/L, and the moisture of the concentration of the metallic oxide in which the desirable presentation in the case of making the layer of the hydrophilic metallic oxide which does not have an opening which reaches a photocatalyst layer cover is converted from an organic metallic compound or its hydrolyzate ] 0.01 to 20 % of the weight 0.01 to 0.6% of the weight.

[0075]Hereafter, a described method (C) is explained. The metallic-oxide overcoat layer in a method (C) is fundamentally the same as a method (B) except the organic high polymer not being added.

[0076]Although the organic high polymer is not included, the liquid which added organic polymer particles, made distribute these, and was fundamentally obtained in the same coating fluid for overcoat formation as a method (B) is applied and dried on said substrate formed [ photocatalyst layer ], The uneven layer of island shape, the shape of a film in which the hole opened, or mesh shape, or the overcoat layer of uneven shape covered thoroughly is obtained by heating at further 350-650 \*\* for for 5 minutes to 2 hours, and decomposing the added organic polymer particles.

[0077]Although it can be used [ any of thermoplasticity and thermosetting resin, or ] as construction material of the above-mentioned organic polymer particles, acrylic resin and styrene resin can use it conveniently especially.

[0078]Although the particle diameter in particular of organic polymer particles is not limited, it is preferred that it is 0.01-50 micrometers. The overcoat layer of a desirable gestalt can be

formed by using the particles of the particle diameter of this range.

[0079]The quantity of the organic polymer particles added in the liquid for overcoat formation is added 300 or less % of the weight 5% of the weight or more to the metallic-oxide conversion total solids in liquid. If there are few additions than 5 % of the weight, it is not enough, and concavo-convex morphogenesis cannot contribute to improvement in hydrophilic nature and also antifog antifouling performance, and is not preferred. Since organic polymer particles will become so much required and cost will start too much in order for film formation efficiency to produce bad desirable overcoat if there are more additions than 300 % of the weight, it is not desirable too.

[0080]As explained by said method (A) and (B), by adding a lot of acid also by a method (C) in the liquid containing an organic metallic compound, the intensity of the film after membrane formation increases remarkably, and the film to which desiccation at low temperature (room temperature -250 \*\*) can also be equal to practical use enough may be obtained.

[0081]The desirable presentation (however, since organic polymer particle content is ending with description, it is removed) of the coating fluid in which increase of such film strength is accepted, Acid is [ 0.0001-2.0mol/L, and the moisture of the concentration of the metallic oxide converted from an organic metallic compound or its hydrolyzate ] 0.001 to 20 % of the weight 0.00001 to 0.6% of the weight like the presentation indicated in the described method (B). The desirable presentation in the case of making the layer of the hydrophilic metallic oxide which does not have the desirable presentation in the case of making the layer of a hydrophilic metallic oxide cover with the state of having an opening which reaches a photocatalyst layer, and an opening which reaches a photocatalyst layer cover is the same as the presentation indicated in the described method (B).

[0082]This invention is applicable to the base material surface of glass, ceramics, a plastic, or metal. The antifog article which prevents the cloudy weather of a substrate, and waterdrop formation in more detail, the antifouling article which prevents the surface from becoming dirty or carries out self-consecration of the surface, It is suitable for articles, such as the windowpane, the mirror, the lens, heat exchanger fins for air conditioners, building materials, a biomechanical material, a film sheet, a showcase, etc. which are especially used as the object for construction, the object for vehicles, the object for optics, industrial use, the object for agriculture, the object for daily needs, the object for residences, and medical application, and has antifog [ good ] or antifouling performance over a long period of time.

[0083]

[Embodiment of the Invention]Hereafter, although this invention is explained in detail based on an example, this invention is not limited only to this example.

[0084][Example 1, the comparative example 1]

[Formation of an alkali filter layer (silica membrane)] Ethanol 96.2 weight section and hydrolyzed-condensation-polymerization liquid (trade name: HAS-10, col coat incorporated company make, 10 % of the weight of silica content) 3.8 weight section of ethyl silicate are mixed at a room temperature, By agitating for 1 hour, the coating fluid for alkali interception silica membrane formation was obtained.



[0085]With cerium oxide system abrasive soap, wash, clean ultrasonically in pure water further and a surface polish and the dry soda lime silicate glass plate (150x150x3 mm) 20 \*\*, It hung vertically under the environment of 30%RH, the above-mentioned coating fluid for alkali interception silica membrane formation was poured from the upper bed of the above-mentioned glass plate, and the single-sided surface of the glass plate was coated with the film (the flow coating method). The glass substrate in which alkali interception silica membrane about 30 nm thick was formed was obtained by drying this glass plate for 30 minutes at 100 \*\*, and heat-treating after desiccation and within 500 \*\* oven for 30 minutes at 250 more \*\* for 1 hour.

[0086][Formation of a photocatalyst layer (titanium oxide thin film)] 60.3 g (0.6 mol) of acetylacetones (AcAc) are gradually dropped using buret, agitating to 85.6 g (0.3 mol) titanium tetraisopropoxide ( $\text{Ti}(\text{OiPr})_4$ ), It agitated for about 1 hour and the stable  $\text{Ti}(\text{AcAc})_2(\text{OiPr})_2$  complex solution was obtained (mother liquor). This mother liquor was diluted with ethanol 1.5 times, and it was considered as the coating solution. The film was made to form at the raising speed for 4.6-cm/after immersing the glass substrate in which the above-mentioned alkali interception silica membrane was formed, into coating fluid, and calcination was performed for 30 minutes at 500 \*\*. Let the obtained sample be the sample A (a glass substrate / alkali interception silica membrane / titanium oxide membrane: comparative example 1). It was checked as a result of analysis by an X diffraction that the titanium oxide membrane of the sample A is an anatase crystal. The thickness of the titanium oxide thin film of the sample A was about 100 nm. As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the titanium oxide membrane of the sample A is less than 0.2 nm, and the concavo-convex average interval (Sm) had become a smooth surface which is 600 nm.

[0087][Formation of an overcoat layer (silica membrane)] By the method described below, the rugged form silica overcoat layer was formed on the sample A. 98.8 g of ethanol, and the hydrolyzed-condensation-polymerization liquid (trade name: -- HAS-10 and col coat incorporated company make.) of ethyl silicate 10 % of the weight per part of silica [ 0.7 g of ] and 0.5 g of chain silica colloid (the average diameter of about 15 nm, the average length of about 170 nm, a trade name: SNOWTEX OUP, the Nissan Chemical Industries, Ltd. make, 15 % of the weight of solid content) were mixed, and coating fluid was obtained by agitating at a room temperature for about 1 hour. In coating fluid, ethyl silicate converted into the silica for binders, and contained at a rate of 93% by the weight ratio to the silica particle. The sample A board was vertically hung under the environment of 20 \*\* and 30%RH, the above-mentioned coating fluid for overcoat layer formation was poured from the upper bed of the above-mentioned substrate, and the overcoat film was coated on the photocatalyst layer of a substrate (the flow coating method). Then, the sample B (a glass substrate / alkali interception silica membrane / titanium oxide membrane / rugged-form silica overcoat layer: example 1) was obtained by heat-treating at 500 \*\* for 1 hour. As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample B is 8 nm, and the concavo-convex average interval (Sm) had become an irregular surface which is 30

nm. When asked for the average thickness of this silica overcoat layer by ESCA, it was about 15 nm.

[0088][Fog resistance evaluation] Although direct sunlight did not hit, it was indirectly bright in daylight, and neglecting the above-mentioned samples A and B was continued to the interior of a room of the room which people frequent continuously, and the cloudy weather grade when expiration is blown estimated the grade to which the surface becomes dirty and fog resistance falls (expiration test). That is, even if the sample immediately after making the surface clarification blows expiration, it does not produce cloudy weather, but the dirt component in the atmosphere sticks to a sample surface by indoor neglect, and it comes to bloom cloudy by an expiration test. Time (antifog maintaining time) after beginning indoor neglect until cloudy weather begins to arise was made into the index of antifog maintenance nature. It can be said that antifog maintenance nature is high, so that this value is large. The antifog maintenance nature of these samples was evaluated according to the following table 2.

[0089]To the sample (cloudy weather arose by the above-mentioned expiration test) to which fog resistance fell by indoor neglect. It irradiated with xenon lamp light (sample film ultraviolet-ray-intensity [ each ]  $0.5\text{mW}/\text{cm}^2$ : measure with the ultraviolet ray intensity meter by TOPCON CORP. "UVR-2/UD-36".) continuously from the film surface for 1 hour, and the size of the waterdrop angle-of-contact fall was made into the index of antifog recoverability. The ultraviolet-rays (340-395 nm) irradiation intensity of  $0.5\text{ mW}/\text{cm}^2$  is equivalent to about 20% of the ultraviolet ray intensity contained in the direct sunlight from north latitude 35-degree outdoor sunlight by winter, fine weather, and noon. By these ultraviolet rays, if a waterdrop angle of contact falls, it can be said that that sample has very good antifog recoverability. Using an angle-of-contact meter ("CA-DT" by harmony interface science incorporated company), before the optical exposure of 1 hour, and the back, The angle of contact over 0.4 mg of waterdrop was measured, by UV irradiation, the angle of contact asked for the waterdrop angle-of-contact factor which defines which fell by the value of (cosine-1 of angle of contact after the optical exposure of 1 hour)/(cosine-1 of the angle of contact before an optical exposure), and evaluation of antifog recoverability was performed according to the following table 3. It can be said that it excels in the antifog recoverability by optical exposure, so that this waterdrop angle-of-contact factor is small.

[0090]

[Table 2]

----- evaluation Fog resistance sustained period ----- O Less than [ O of \*\* with a / less than nine days / of of six days or more three days or more less than six day x three day ] ----- which the grade which does not bloom cloudy or, out of which some unevenness comes will follow nine days or more[0091]

[Table 3]

----- antifog recoverability Waterdrop angle-of-contact factor Evaluation (cosine-1 of waterdrop angle of contact 1 hour after optical exposure)/(\*\* shooting cosine-of a front waterdrop angle of contact 1)

----- O More than less than [ less than 0.1 O / 0.3 or more / less than / 0.1 or more / 0.3 \*\* ] 0.5 x 0.5 -----[0092]The various evaluation results of the above-mentioned samples A (comparative example 1) and B (example 1) are shown in Table 4. As for the sample B (example 1), it is distinct that antifog maintenance nature and antifog recoverability are remarkably improved as compared with the sample A (comparative example 1).

[0093]

[Table 4]

----- Sun Antifog Waterdrop angle of contact Fog resistance evaluation Antifouling property PU Maintaining time factor ----- evaluation RU (Sun.) Maintenance nature Recoverability ----- Example one B12.3 0.09 O O. \*\*2 C 9.5 0.15 O O O3. D 9.8 0.43 O \*\* O4 E. 11.0 0.08 OO O5 F 4.5. 0.09 \*\* O O6 G 3.0 0.31. \*\* \*\* \*\*7 H 8.0 0.05 O. O O8 I 9.7 0.15 O O. \*\*9 J 15.3 0.03 O O O10. K 14.7 0.30 O O O11. L 10.3 0.28 O O O12. N 38.3 0.07 O O O13 O 38.2 0.01 O O O14 Q 9.5 0.20 O OO15 R 20.5 0.25 O O O16 S 7.0 0.15 O O O17 W 9.3 0.05 O O O ----- Comparative example one A0.5 0.31 x \*\* x2 T 5.2 0.55 \*\* x \*\*3 U 5.5 0.50 \*\* x \*\*4 V 1.1 0.51 x \*\* \*\*-----

[0094][Antifouling property evaluation] The following outdoor exposure tests performed antifouling property. Sample plates were vertically installed in the outdoors in Itami-shi, Hyogo, the six-month exposure examination in July - December was done under the environment which imitated the vertical plane under the eaves from which storm sewage flows through the sample-plates surface, and falls, and contamination status evaluation of the sample plates after an examination was performed in the visual evaluation by the standard of the following table 5.

[0095]

[Table 5]

----- antifouling property Evaluation Contamination status ----- O Dirt is hardly worrisome. ----- in which x dirt which is a little [ O ] dirty, where muscle-like dirt appears thinly, and with which it \*\* Is dirty and muscle-like dirt is conspicuous is remarkable, and muscle-like dirt is considerably conspicuous[0096]The antifouling property evaluation result of the above-mentioned samples A (comparative example 1) and B (example 1) is shown in Table 4. As for the sample B (example 1), it is distinct that antifouling property is remarkably improved as compared with the sample A (comparative example 1).

[0097][Example 2]

[Formation of an overcoat layer (silica membrane)] By the method described below, the rugged form silica overcoat layer was formed on the sample A produced in Example 1. 99.94 g of 2-propanol -- the hydrolyzed-condensation-polymerization liquid (trade name: -- HAS-10 and col coat incorporated company make.) of ethyl silicate 10 % of the weight of silica content of 0.3 g and 0.3 g of silica colloid (trade name: IPA-ST, the Nissan Chemical Industries, Ltd. make, particle diameter of 10-20 nm, 30 % of the weight of silica content) were added, and coating fluid was obtained by agitating at a room temperature for about 1 hour. In coating fluid, ethyl silicate converted into the silica for binders, and contained at a rate of 33% by the weight ratio

to the silica particle. The silica overcoat thin film was made to form by applying the above-mentioned coating fluid on the sample A by the same method as the method of example 1 statement, and drying for 30 minutes at 100 \*\*. Thus, the obtained sample is set to C (a glass substrate / alkali interception silica membrane / titanium oxide membrane / rugged form silica overcoat thin film). As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample C is 12 nm, and the concavo-convex average interval (Sm) had become an irregular surface which is 150 nm. When asked for the average thickness of this silica overcoat layer by ESCA, it was about 10 nm.

[0098]The various antifog antifouling quality assessment results of the sample C are shown in Table 4. Compared with the comparative example 1, it is distinct that the antifog antifouling performance is improving.

[0099][Example 3]

[Formation of an overcoat layer (alumina silica membrane)] By the method described below, the rugged form overcoat layer was formed on the sample A produced in Example 1. 0.25 g of tetraethoxysilanes and 0.2 g of alumina colloid (trade name: the alumina sol 520, the Nissan Chemical Industries, Ltd. make, particle diameter of 40-50 nm, 20% of alumina content) were added to 99.71 g of ethanol, and coating fluid was obtained by agitating at a room temperature for about 1 hour. In coating fluid, the binder of tetraethoxysilane origin contained at a rate of 180% to the alumina particle by silica conversion at the weight ratio. The alumina silica overcoat thin film was made to form by applying by the same method as the method of example 1 statement, and heat-treating for 30 minutes at 250 \*\*. Thus, the obtained sample is set to D (a glass substrate / alkali interception silica membrane / titanium oxide membrane / rugged form overcoat thin film). As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample D is 3 nm, and the concavo-convex average interval (Sm) had become an irregular surface which is 300 nm. When the average thickness of this overcoat layer was measured by ESCA, it was about 10 nm.

[0100]The various antifog antifouling quality assessment results of the sample D are shown in Table 4. Compared with the comparative example 1, it is distinct that the antifog antifouling performance is improving.

[0101][Example 4]

[Formation of an overcoat layer (titania silica membrane)] By the method described below, the rugged form overcoat layer was formed on the sample A produced in Example 1. They are 1.34 g of tetrachlorosilicane, and titania colloid (trade name:) to 997.21 g of ethanol. [ CS-N and ] The Ishihara Sangyo Kaisha, Ltd. make, the particle diameter of 30-60 nm, the titania 30-% of the weight content of 0.45 g, 1.0 g of chain silica colloid (the average diameter of about 15 nm, the average length of about 170 nm, a trade name: SNOWTEX OUP, the Nissan Chemical Industries, Ltd. make, 15 % of the weight of solid content) was added, it agitated at the room temperature for about 1 hour, and coating fluid was obtained. In coating fluid, the binder of tetrachlorosilicane origin contained at a rate of 166% to the sum total of titania particles and a silica particle by silica conversion at the weight ratio. The titania silica overcoat thin film was made to form by applying by the same method as the method of example 1

statement, and drying at a room temperature. Thus, let the obtained sample be the sample E (a glass substrate / alkali interception silica membrane / titanium oxide membrane / rugged form overcoat thin film). As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample E is 35 nm, and the concavo-convex average interval (Sm) had become an irregular surface which is 40 nm. When asked for the average thickness of this overcoat layer by ESCA, it was about 8 nm.

[0102]The various antifog antifouling quality assessment results of the sample E are shown in Table 4. It is clear to have the outstanding antifog antifouling performance.

[0103][Example 5]

[Formation of an overcoat layer (silica membrane)] By the method described below, the mesh shape silica overcoat layer was formed on the sample A produced in Example 1. 99.94 g of 2-propanol -- the hydrolyzed-condensation-polymerization liquid (trade name: -- HAS-10 and col coat incorporated company make.) of ethyl silicate 10 % of the weight of silica content of 0.03 g and 0.03 g of silica colloid (trade name: IPA-ST, the Nissan Chemical Industries, Ltd. make, particle diameter of 10-20 nm, 30 % of the weight of silica content) were added, and coating fluid was obtained by agitating at a room temperature for about 1 hour. In coating fluid, ethyl silicate converted into the silica for binders, and contained at a rate of 33% by the weight ratio to the silica particle. The silica overcoat thin film was made to form by applying the above-mentioned coating fluid on the sample A by the same method as the method of example 1 statement, and drying for 30 minutes at 100 \*\*. Thus, the obtained sample is set to F (a glass substrate / alkali interception silica membrane / titanium oxide membrane / mesh shape silica overcoat thin film). As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample F is 5 nm, and the concavo-convex average interval (Sm) had become an irregular surface which is 100 nm. When the surface of the sample F was observed with the electron microscope, silica overcoat is mesh shape (average diameter of about 100 nm of the hole of meshes of a net), and the photocatalyst layer of the ground was observed. It became clear by using image-analysis art that it had exposed without covering about 50% of photocatalyst layer surface area with silica. When asked for the average thickness of this silica overcoat layer by ESCA, it was about 2 nm.

[0104]The various antifog antifouling quality assessment results of the sample F are shown in Table 4. Compared with the comparative example 1, it is distinct that the antifog antifouling performance is improving.

[0105][Example 6]

[Formation of an overcoat layer (alumina silica membrane)] By the method described below, the mesh shape overcoat layer was formed on the sample A produced in Example 1. 0.25 g of tetraethoxysilanes and 0.2 g of alumina colloid (trade name: the alumina sol 520, the Nissan Chemical Industries, Ltd. make, particle diameter of 40-50 nm, 20% of alumina content) were added to 99.71 g of ethanol, and it agitated at the room temperature for about 1 hour, and was considered as the undiluted solution. Coating fluid was obtained by diluting this undiluted solution with ethanol 100 times. In coating fluid, the binder of tetraethoxysilane origin contained at a rate of 180% to the alumina particle by silica conversion at the weight ratio. The alumina

silica overcoat thin film was made to form by applying by the same method as the method of example 1 statement, and heat-treating for 30 minutes at 250 \*\*. Thus, the obtained sample is set to G (a glass substrate / alkali interception silica membrane / titanium oxide membrane / mesh shape overcoat thin film). As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample G is 0.6 nm, and the concavo-convex average interval (Sm) had become an irregular surface which is 300 nm. When the surface of the sample G was observed with the electron microscope, overcoat is mesh shape (average diameter of about 1000 nm of the hole of meshes of a net), and the photocatalyst layer of the ground was observed. It became clear by using image-analysis art that it had exposed without covering about 80% of photocatalyst layer surface area with an overcoat layer. When the average thickness of this overcoat layer was guessed from coating fluid concentration, it was about 0.1 nm.

[0106]The various antifog antifouling quality assessment results of the sample G are shown in Table 4. Compared with the comparative example 1, it is distinct that the antifog antifouling performance is improving.

[0107][Example 7]

[Formation of an overcoat layer (zirconia silica membrane)] By the method described below, the mesh shape overcoat layer was formed on the sample A produced in Example 1. Alcohol (85.5 % of the weight of ethanol and 9.6 % of the weight of 1-propanol) 4.9 % of the weight of 2-propanol, trade name:AP-7, and the Nippon Kasei Chemical article incorporated company make 99.33g -- the hydrolyzed-condensation-polymerization liquid (trade name: -- HAS-10 and col coat incorporated company make.) of ethyl silicate 10 % of the weight of silica content of 0.50 g and 0.17 g of zirconia colloid (trade name: NZS-30A, the Nissan Chemical Industries, Ltd. make, particle diameter of 40-50 nm, 30% of zirconia content) were added, and it agitated at the room temperature for about 1 hour, and was considered as the undiluted solution. The solution made to dissolve a 0.01-g aluminium chloride in 500 g of ethanol was produced independently, and coating fluid was obtained by diluting a previous undiluted solution with this solution 5 times. In coating fluid, the binder of ethyl silicate origin contained at a rate of 98% to zirconia particles by silica conversion at the weight ratio. The zirconia silica overcoat thin film was made to form by applying by the same method as the method of example 1 statement, and heat-treating at 500 \*\* for 1 hour. Thus, the obtained sample is set to H (a glass substrate / alkali interception silica membrane / titanium oxide membrane / mesh shape overcoat thin film). As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample H is 8 nm, and the concavo-convex average interval (Sm) had become an irregular surface which is 80 nm. When the surface of the sample H was observed with the electron microscope, overcoat is mesh shape (average diameter of about 90 nm of the hole of meshes of a net), and the photocatalyst layer of the ground was observed. It became clear by using image-analysis art that it had exposed without covering about 50% of photocatalyst layer surface area with overcoat. When asked for the average thickness of this overcoat layer by ESCA, it was about 2 nm.

[0108]The various antifog antifouling quality assessment results of the sample H are shown in

Table 4. It is clear to have the outstanding antifog antifouling performance.

[0109][Example 8]

[Formation of an overcoat layer (titania silica membrane)] By the method described below, the film-like overcoat layer in which the hole opened was formed on the sample A produced in Example 1. They are 1.34 g of tetrachlorosilicane, and titania colloid (trade name:) to 498.21 g of ethanol. [ CS-N and ] The Ishihara Sangyo Kaisha, Ltd. make, the particle diameter of 30-60 nm, 30 % of the weight of titania content of 0.45 g, and 0.002 g of iron(III) chlorides were added, it agitated at the room temperature for about 1 hour, and coating fluid was obtained. In coating fluid, the binder of tetrachlorosilicane origin contained at a rate of 351% to titania particles by silica conversion at the weight ratio. The titania silica overcoat thin film was made to form by applying by the same method as the method of example 1 statement, and drying at a room temperature. Thus, the obtained sample is set to I (film-like overcoat thin film in which a glass substrate / alkali interception silica membrane / titanium oxide membrane / hole opened). As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample I is 30 nm, and the concavo-convex average interval (Sm) had become an irregular surface which is 50 nm. When the surface of the sample I was observed with the electron microscope, overcoat is the shape of a film in which the hole opened (average diameter of about 40 nm of a hole), and the photocatalyst layer of the ground was observed. It became clear by using image-analysis art that it had exposed without covering about 30% of photocatalyst layer surface area with overcoat. When asked for the average thickness of this overcoat layer by ESCA, it was about 10 nm.

[0110]The various antifog antifouling quality assessment results of the sample I are shown in Table 4. It is clear to have the outstanding antifog antifouling performance.

[0111][Example 9]

[Formation of an overcoat layer (vanadium compound addition silica membrane)] By the method described below, the mesh shape silica overcoat layer was formed on the sample A produced in Example 1. 0.12 g of concentrated hydrochloric acid and 1.23 g of alcohol (trade name: AP-7, the Nippon Kasei Chemical article incorporated company make) were added, it dissolved, and 0.15 g of acetylacetone vanadyl was used as vanadium addition liquid. 0.14 g of tetrachlorosilicane and the above-mentioned vanadium addition liquid 1.46g were added to 98.40 g of alcohol (trade name: AP-7, the Nippon Kasei Chemical article incorporated company make), and coating fluid was obtained by agitating at a room temperature for about 1 hour. The vanadium compound addition silica overcoat thin film was made to form by applying by the same method as the method of example 1 statement, and heat-treating at 450 \*\* for 1 hour. Thus, the obtained sample is set to J (a glass substrate / alkali interception silica membrane / titanium oxide membrane / vanadium compound addition silica overcoat thin film). As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample J is 50 nm, and the concavo-convex average interval (Sm) had become an irregular surface which is 50 nm. When the surface of the sample J was observed with the electron microscope, overcoat is mesh shape (average diameter of about 30 nm of the hole of meshes of a net), and the photocatalyst layer of the ground was observed. It

became clear by using image-analysis art that it had exposed without covering about 40% of photocatalyst layer surface area with overcoat. When asked for the average thickness of this overcoat layer by ESCA, it was about 7 nm.

[0112]The various antifog antifouling quality assessment results of the sample J are shown in Table 4. It is clear to have the outstanding antifog antifouling performance.

[0113][Example 10]

[Formation:polymer particulate addition method which is an overcoat layer (silica membrane)] 76.53 g of ethanol and the 0.1N chloride 0.70g were added to 3.00 g of tetraethoxysilanes, it agitated for about 1 hour, and 1650 g of ethanol was added and diluted further. 5.0 g of polymethylmethacrylate particle water dispersing elements (trade name: MA03W, the Nippon Shokubai Kagaku Kogyo Co., Ltd. make, mean particle diameter of 0.03 micrometer, 10 % of the weight of particle content) were added in this solution, and it mixed for 1 hour, and was considered as coating fluid. In coating fluid, polymethylmethacrylate particles contained at a rate of about 58% by the weight ratio to the binder of tetraethoxysilane origin (silica conversion).

[0114]On the sample A produced in Example 1, membranes were formed so that silica membrane thickness might be set to 30 nm by the spin coating method (1000 rpm, 10 seconds, volume of 4 ml), and it dried at the room temperature. In order to burn acrylic particles and to elaborate silica membrane, the silica overcoat thin film was made to form by calcinating at 550 more \*\* for 1 hour. Thus, the obtained sample is set to K (a glass substrate / alkali interception silica membrane / titanium oxide membrane / rugged form silica overcoat thin film). As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample K is 30 nm, and the concavo-convex average interval (Sm) had become an irregular surface which is 30 nm. When asked for the average thickness of this overcoat layer by ESCA, it was about 25 nm.

[0115]The various antifog antifouling quality assessment results of the sample K are shown in Table 4. It is clear to have the outstanding antifog antifouling performance.

[0116][Example 11]

[Formation:polymer particulate addition method which is an overcoat layer (silica membrane)] 76.53 g of ethanol and the 0.1N chloride 0.70g were added to 3.00 g of tetraethoxysilanes, it agitated for about 1 hour, and 1650 g of ethanol was added and diluted further. Added 0.17 g of acrylic particle impalpable powder (trade name: GL300, the Soken Chemical & Engineering, Inc. make, acrylic particles bridge construction type [ with a particle diameter of 0.1 micrometer ]) in this solution, the homogenizer was made to distribute, and it was considered as coating fluid. In coating fluid, acrylic particles contained at a rate of about 20% by the weight ratio to the binder of tetraethoxysilane origin (silica conversion).

[0117]On the sample A produced in Example 1, membranes were formed so that silica membrane thickness might be set to 30 nm by the spin coating method (1000 rpm, 10 seconds, volume of 4 ml), and it dried at the room temperature. In order to burn acrylic particles and to elaborate silica membrane, the silica overcoat thin film was made to form by calcinating at 600 more \*\*. Thus, the obtained sample is set to L (film-like silica overcoat thin



film in which a glass substrate / alkali interception silica membrane / titanium oxide membrane / hole opened). As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample L is 15 nm, and the concavo-convex average interval (Sm) had become an irregular surface which is 200 nm. When the surface of the sample L was observed with the electron microscope, overcoat is the shape of a film in which the hole opened (average diameter of about 100 nm of a hole), and the photocatalyst layer of the ground was observed. It became clear by using image-analysis art that it had exposed without covering about 15% of photocatalyst layer surface area with overcoat. When asked for the average thickness of this overcoat layer by ESCA, it was about 20 nm.

[0118]The various antifog antifouling quality assessment results of the sample L are shown in Table 4. It is clear to have the outstanding antifog antifouling performance.

[0119][Example 12]

[Formation of an alkali interception film (silica zirconia thin film)] Zirconium butoxide 5 weight section was added to ethyl acetoacetate 1 weight section, and it agitated at 30 °C for 2 hours. Let this be A liquid. On the other hand, tetraethoxysilane 50 weight section, 2-propanol 1000 weight section, nitric acid 2.5 weight section of 1N, and water 50 weight section were added to according to, and it agitated at 30 °C for 2 hours. Let this be B liquid. mixing A liquid and B liquid and carrying out churning care of health for one day at 30 °C more at 50 °C for 3 hours, respectively -- the object for alkali interception films -- sol -- liquid was obtained.

[0120]the soda lime silicate glass plate (65mmx150mmx3mm) which a surface polish and washing of were done with cerium oxide system abrasive soap, and was further cleaned ultrasonically and dried in pure water -- the above-mentioned object for an alkali interception film -- sol -- it was immersed in liquid, the glass plate was pulled up the speed for 10-cm/, and sol was applied. Then, this was dried for several minutes at the room temperature, it heat-treated at 500 °C for 3 hours, and the glass plate with which the silica zirconia thin film (92 % of the weight of silica, 8 % of the weight of zirconia) about 30 nm thick was formed was obtained.

[0121][Formation of a vanadium compound addition titanium oxide particle distribution silica film] Next, the coating method of the vanadium addition titanium oxide particle distribution silica film by a sol gel process is explained. 0.79 g of 35% chloride and 8.21 g of alcohol (trade name: AP-7, the Nippon Kasei Chemical article incorporated company make) were added to 1.00 g of acetylacetone vanadyl, and it dissolved in it, and was considered as vanadium addition liquid. 0.34 g of tetrachlorosilane, 2.00 g of titania-particles dispersion liquid (trade name: ST-K01, Ishihara Sangyo Kaisha, Ltd. make), and said 2.66 g of vanadium addition liquid are added to 95.00 g of alcohol (trade name: AP-7, the Nippon Kasei Chemical article incorporated company make), Coating fluid was obtained by mixing at a room temperature for about 2 hours. After forming a film in a soda lime silicate glass substrate with the above-mentioned silica zirconia membrane by the flow coating method of example 1 statement using this coating fluid, by heat-treating at desiccation and 500 °C with a room temperature for 1 hour, The sample M (a glass substrate / silica zirconia thin film / vanadium compound addition

titanium oxide particle distribution silica film) was obtained.

[0122]The vanadium oxide addition titanium oxide particle distribution silica film of the sample M had a thickness of about 60 nm, consisted of a presentation of 39 % of the weight of oxidized silicon, 39 % of the weight of titanium oxide, and 22 % of the weight of vanadium compounds ( $V_2O_5$  conversion), and was V/Ti=0.5 (atomic ratio).

[0123][Formation of an overcoat layer (silica membrane)] On the sample M, the silica overcoat layer was formed by the method described below. 98.9 g of ethanol, and the hydrolyzed-condensation-polymerization liquid (trade name: -- HAS-10 and col coat incorporated company make.) of ethyl silicate 10 % of the weight per part of silica [ 0.5 g of ] and 0.6 g of chain silica colloid (the average diameter of about 15 nm, the average length of about 170 nm, a trade name: SNOWTEX OUP, the Nissan Chemical Industries, Ltd. make, 15 % of the weight of solid content) were mixed, and coating fluid was obtained by agitating at a room temperature for about 1 hour. In coating fluid, ethyl silicate converted into the silica for binders, and contained at a rate of about 56% by the weight ratio to the silica particle.

[0124]By the flow coat method of example 1 statement, and the same method, coat the sample M surface with the above-mentioned coating fluid, and it heat-treats at 500 \*\* for 1 hour, The sample N (a glass substrate / silica zirconia thin film / vanadium-oxide addition titanium-oxide particle distribution silica film / concavo-convex silica overcoat layer: example 12) was obtained. As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample N is 40 nm, and the concavo-convex average interval (Sm) had become an irregular surface which is 70 nm. When asked for the average thickness of this silica overcoat layer by ESCA, it was about 15 nm. The various antifog antifouling quality assessment results of the sample N (example 12) are shown in Table 4. It is clear to have the antifog antifouling property more outstanding by rugged form silica overcoat layer formation.

[0125][Example 13]

[Formation of an overcoat layer (silica membrane)] On the sample M obtained in Example 12, the silica overcoat layer was formed by the method described below. 99.1 g of ethanol, and the hydrolyzed-condensation-polymerization liquid (trade name: -- HAS-10 and col coat incorporated company make.) of ethyl silicate 10 % of the weight per part of silica [ 0.7 g of ] and 0.2 g of chain silica colloid (the average diameter of about 15 nm, the average length of about 170 nm, a trade name: SNOWTEX OUP, the Nissan Chemical Industries, Ltd. make, 15 % of the weight of solid content) were mixed, and coating fluid was obtained by agitating at a room temperature for about 1 hour. In coating fluid, ethyl silicate converted into the silica for binders, and contained at a rate of 232% by the weight ratio to the silica particle.

[0126]By the flow coat method of example 1 statement, and the same method, coat the sample M surface with the above-mentioned coating fluid, and it heat-treats at 500 \*\* for 1 hour, The sample O (a glass substrate / silica zirconia thin film / vanadium-oxide addition titanium-oxide particle distribution silica film / silica overcoat layer: example 13) was obtained. As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample O is 30 nm, and the concavo-convex average interval (Sm) had become

an irregular surface which is 85 nm. When the surface of the sample O was observed with the electron microscope, silica overcoat is the shape of a film in which the hole opened (average diameter of about 30 nm of a hole), and the photocatalyst layer of the ground was observed. It became clear by using image-analysis art that it had exposed without covering about 30% of photocatalyst layer surface area with silica. When asked for the average thickness of this silica overcoat layer by ESCA, it was about 10 nm. The various antifog antifouling quality assessment results of the sample O (example 13) are shown in Table 4. It is clear to have the antifog antifouling property more outstanding by silica overcoat layer formation of the shape of a film in which the hole opened.

[0127][Example 14]

[Formation of an alkali interception film (silica titania thin film)] Titanium isopropoxide 2.8 weight section was added to the amount part of acetylacetone duplexs, and it agitated at 30 \*\* for 2 hours. Let this be A liquid. On the other hand, tetraethoxysilane 50 weight section, 2-propanol 1000 weight section, nitric acid 2.5 weight section of 1N, and water 50 weight section were added to according to, and it agitated at 30 \*\* for 2 hours. Let this be B liquid. mixing A liquid and B liquid and carrying out churning care of health for one day at 30 more \*\* at 50 \*\* for 3 hours, respectively -- the object for alkali interception films -- sol -- liquid was obtained.

[0128]the soda lime silicate glass plate (65mmx150mmx3mm) which a surface polish and washing of were done with cerium oxide system abrasive soap, and was further cleaned ultrasonically and dried in pure water -- the above-mentioned object for an alkali interception film -- sol -- it was immersed in liquid, the glass plate was pulled up the speed for 10-cm/, and sol was applied. Then, this was dried for several minutes at the room temperature, it heat-treated at 500 more \*\* for 3 hours, and the glass plate with which the silica titania thin film (96 % of the weight of silica, 4 % of the weight of titanias) about 30 nm thick was formed was obtained.

[0129][Formation of photocatalyst membrane (titania-particles distribution silica film)]

Photocatalyst coating liquid ST-K03 (the Ishihara Sangyo Kaisha, Ltd. make, 5 % of the weight of titanium oxide particle content, 5 % of the weight of inorganic binders) of marketing was diluted 4 weight twice using ethanol. On the glass plate in which said silica titania thin film was formed, this liquid was formed by the spin coating method (1500 rpm, 10 seconds, volume of 4 ml), it heat-treated at 520 \*\* for 1 hour, and the photocatalyst thin film of about 60-nm thickness was formed. It checked that this photocatalyst thin film consisted of about 50 % of the weight of titanium oxide, and about 50 % of the weight of oxidized silicon as a result of the chemical analysis.

[0130]Let the obtained sample be the sample P (a glass substrate / alkali interception silica titania thin film / titanium oxide particle distribution silica film). It was checked as a result of analysis by an X diffraction that the titanium oxide membrane of the sample P is an anatase crystal. As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample P is 2 nm, and the concavo-convex average interval (Sm) had become an irregular surface which is 60 nm.

[0131][Formation of an overcoat layer (silica membrane)] The island-shape silica overcoat

layer of the example 1 statement was formed by the method of the example 1 statement on the sample P. Let the obtained sample be the sample Q (a glass substrate / alkali interception silica titania thin film / titanium-oxide particle distribution silica film / island-shape silica overcoat layer: example 14). As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample Q is 15 nm, and the concavo-convex average interval (Sm) had become an irregular surface which is 50 nm. When the surface of the sample Q was observed with the electron microscope, silica overcoat is island shape (average diameter of about 50 nm of the bottom of an island), and the photocatalyst layer of the ground was observed. It became clear by using image-analysis art that it had exposed without covering about 40% of photocatalyst layer surface area with silica overcoat. When asked for the average thickness of this silica overcoat layer by ESCA, it was about 5 nm.

[0132]The various evaluation results of the above-mentioned sample Q (example 14) are shown in Table 4. It is clear the sample's Q (example 14) to have the outstanding antifog maintenance nature and antifog recoverability.

[0133][Example 15]

[Formation:organic high polymer addition method which is an overcoat layer (silica membrane)] By the method described below, the rugged form silica overcoat layer was formed on the sample A produced in Example 1. 100 g of ethanol, 5.4 g of hydrolyzed-condensation-polymerization liquid (trade name: HAS-10, col coat incorporated company make, silica 10 % of the weight per part) of ethyl silicate, and 1.2 g of polyethylene glycols (average molecular weight 1000) were mixed, and coating fluid was obtained by agitating at a room temperature for about 1 hour. In coating fluid, the polyethylene glycol contained at a rate of about 222% by the weight ratio to the binder of ethyl silicate origin (silica conversion). By the method as the method of example 1 statement that it is the same on a sample A board, coating fluid coating was carried out [ above-mentioned ] for overcoat layer formation. Then, the sample R (a glass substrate / alkali interception silica membrane / titanium oxide membrane / rugged form silica overcoat layer) was obtained by heat-treating at 520 \*\* for 1 hour. As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample R is 70 nm, and the concavo-convex average interval (Sm) had become an irregular surface which is 50 nm. When asked for the average thickness of this silica overcoat layer by ESCA, it was about 45 nm.

[0134]The various antifog antifouling quality assessment results of the sample R are shown in Table 4. It is clear to have the outstanding antifog antifouling performance.

[0135][Example 16]

[Formation:organic high polymer addition method which is an overcoat layer (silica membrane)] By the method described below, the film-like silica overcoat layer in which the hole opened was formed on the sample A produced in Example 1. 280 g of ethanol, 1.4 g of hydrolyzed-condensation-polymerization liquid (trade name: HAS-10, col coat incorporated company make, silica 10 % of the weight per part) of ethyl silicate, and 0.3 g of polyethylene glycols (average molecular weight 400) were mixed, and coating fluid was obtained by

agitating at a room temperature for about 1 hour. In coating fluid, the polyethylene glycol contained at a rate of about 214% by the weight ratio to the binder of ethyl silicate origin (silica conversion). By the method as the method of example 1 statement that it is the same on a sample A board, coating fluid coating was carried out [ above-mentioned ] for overcoat layer formation. Then, the sample S (film-like silica overcoat layer in which a glass substrate / alkali interception silica membrane / titanium oxide membrane / hole opened) was obtained by heat-treating at 520 °C for 1 hour. As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample S is 70 nm, and the concavo-convex average interval (Sm) had become an irregular surface which is 150 nm. When the surface of the sample S was observed with the electron microscope, silica overcoat is the shape of a film in which the hole opened (average diameter of about 50 nm of a hole), and the photocatalyst layer of the ground was observed. It became clear by using image-analysis art that it had exposed without covering about 60% of photocatalyst layer surface area with silica. When asked for the average thickness of this silica overcoat layer by ESCA, it was about 8 nm.

[0136]The various antifog antifouling quality assessment results of the sample S are shown in Table 4. It is clear to have the outstanding antifog antifouling performance.

[0137][Example 17]

[Formation of an overcoat layer (silica membrane)] By the method described below, the island-shape silica overcoat layer was formed on the sample A produced in Example 1. 280 g of ethanol, and the hydrolyzed-condensation-polymerization liquid (trade name: -- HAS-10 and col coat incorporated company make.) of ethyl silicate 10 % of the weight per part of silica [ 0.7 g of ] and 0.5 g of chain silica colloid (the average diameter of about 15 nm, the average length of about 170 nm, a trade name: SNOWTEX OUP, the Nissan Chemical Industries, Ltd. make, 15 % of the weight of solid content) were mixed, and coating fluid was obtained by agitating at a room temperature for about 1 hour. In coating fluid, ethyl silicate converted into the silica for binders, and contained at a rate of 93% by the weight ratio to the silica particle. The sample A board was vertically hung under the environment of 20 °C and 30%RH, the above-mentioned coating fluid for overcoat layer formation was poured from the upper bed of the above-mentioned substrate, and the overcoat film was coated on the photocatalyst layer of a substrate (the flow coating method). Then, the sample W (a glass substrate / alkali interception silica membrane / titanium oxide membrane / island-shape silica overcoat layer: example 1) was obtained by heat-treating at 500 °C for 1 hour. As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample W is 10 nm, and the concavo-convex average interval (Sm) had become an irregular surface which is 50 nm. When the surface of the sample W was observed with the electron microscope, silica overcoat is island shape (average diameter of about 50 nm of the bottom of an island), and the photocatalyst layer of the ground was observed. It became clear by using image-analysis art that it had exposed without covering about 40% of photocatalyst layer surface area with silica. When asked for the average thickness of this silica overcoat layer by ESCA, it was about 5 nm.

[0138]The various antifog antifouling quality assessment results of the sample W are shown in Table 4. It is clear to have the outstanding antifog antifouling performance.

[0139][Comparative example 2]

[Formation of a smooth overcoat layer (silica membrane)] By the method described below, the smooth silica overcoat layer was formed on the sample A produced in Example 1. 140 g of ethanol and 1.4 g of hydrolyzed-condensation-polymerization liquid (trade name: HAS-10, col coat incorporated company make, silica 10 % of the weight per part) of ethyl silicate were mixed, and coating fluid was obtained by agitating at a room temperature for about 1 hour. By the method as the method of example 1 statement that it is the same on a sample A board, coating fluid coating was carried out [ above-mentioned ] for overcoat layer formation. Then, the sample T (a glass substrate / alkali interception silica membrane / titanium oxide membrane / smooth silica overcoat layer) was obtained by heat-treating at 500 \*\* for 1 hour. As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample T is 0.2 nm or less, and the concavo-convex average interval (Sm) had become a smooth surface which is not less than 400 nm. When asked for the average thickness of this silica overcoat layer by ESCA, it was about 10 nm.

[0140]The various antifog antifouling quality assessment results of the sample T are shown in Table 4. Compared with an example, it is clear that antifog antifouling performance is low.

[0141][Comparative example 3]

[Formation of a smooth overcoat layer (silica membrane)] By the method described below, the smooth silica overcoat layer was formed on the sample A produced in Example 1. 280 g of ethanol and 1.4 g of hydrolyzed-condensation-polymerization liquid (trade name: HAS-10, col coat incorporated company make, silica 10 % of the weight per part) of ethyl silicate were mixed, and coating fluid was obtained by agitating at a room temperature for about 1 hour. By the method as the method of example 1 statement that it is the same on a sample A board, coating fluid coating was carried out [ above-mentioned ] for overcoat layer formation. Then, the sample U (a glass substrate / alkali interception silica membrane / titanium oxide membrane / smooth silica overcoat layer) was obtained by heat-treating at 500 \*\* for 1 hour. As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample U is 0.2 nm or less, and the concavo-convex average interval (Sm) had become a smooth surface which is not less than 400 nm. When the surface of the sample U was observed with the electron microscope, silica overcoat has covered photocatalyst membrane thoroughly and the photocatalyst layer of the ground was not observed. When asked for the average thickness of this silica overcoat layer by ESCA, it was about 5 nm.

[0142]The various antifog antifouling quality assessment results of the sample U are shown in Table 4. Compared with an example, it is clear that antifog antifouling performance is low.

[0143][Comparative example 4] Replace with the formation of an overcoat layer (silica membrane) in Example 1, and with a vacuum deposition method (evaporation rate 0.5nm [// a second and ] and oxygen tension  $2.0 \times 10^{-4}$  torr, substrate temperature 200 \*\*). A 15-nm-thick overcoat layer (silica membrane) is made to form, and also it is the same method as Example

1, and the sample V (a glass substrate / alkali interception silica membrane / titanium oxide membrane / porous silica overcoat layer) was obtained. As a result of measurement by an atomic force microscope, the arithmetic mean roughness (Ra) of the surface of the sample V is 3 nm, and the concavo-convex average interval (Sm) had become an irregular surface which is 150 nm. When the surface of the sample V was observed with the electron microscope, silica overcoat is the shape of a porous membrane which has an independent hole (average diameter of about 0.5 nm of an independent hole), and the photocatalyst layer of the ground was not observed. It became clear by using image-analysis art that it had exposed without covering about 5% of photocatalyst layer surface area with silica. When asked for the average thickness of this silica overcoat layer by ESCA, it was about 15 nm.

[0144]The various antifog antifouling quality assessment results of the sample V are shown in Table 4. It is clear that antifog antifouling performance is not good.

[0145]

[Effect of the Invention]As explained above, since it is clear to have the outstanding antifog antifouling performance and its maintenance nature and mechanical endurance is also good, the glass article of this invention can be used conveniently for the uses the object for cars, the object for construction, for optics, etc.

---

[Translation done.]